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(54) Title: METHOD OF MAKING A PVD $AL_2O_3$ COATED CUTTING TOOL

(57) Abstract

The present invention relates to a process for producing a coated cutting tool consisting of a coating and a substrate, wherein at least one refractory layer consisting of fine–grained, crystalline $\gamma$–$Al_2O_3$ is deposited by reactive magnetron sputtering onto the moving substrate in a vacuum by pulsed magnetron sputtering in a mixture of a rare gas and a reactive gas at a pulse frequency set for 10 to 100 kHz. The deposition occurs with a rate of at least 1 nm/s with reference to a stationarily arranged substrate at a magnetron target power density in time average set for at least 10W/cm$^2$. The substrate temperature is in the range of 400 to 700 °C and the flux of impinging particles onto each individual substrate is cyclically interrupted.

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# METHOD OF MAKING A PVD $Al_2O_3$ COATED CUTTING TOOL

The present invention relates to an improved method of depositing at least one layer of fine-crystalline $\gamma$-$Al_2O_3$ by reactive magnetron sputtering technique onto a cutting tool for metal machining.

It is well known that for e.g. cemented carbide cutting tools used in metal machining, the wear resistance of the tool edge considerably can be increased by applying thin, hard surface layers of metal oxides, carbides or nitrides with the metal either selected from the transition metals from the groups IV, V and VI of the Periodic Table or from silicon, boron and aluminium. The coating thickness usually varies between 1 and 15 µm and the most widespread techniques for depositing such coatings are PVD and CVD (Chemical Vapor Deposition). It is also known that further improvements of the performance of a cutting tool can be achieved by applying a pure ceramic layer such as $Al_2O_3$ on top of layers of metal carbides and nitrides (US 5,674,564 and US 5,487,625).

Cemented carbide cutting tools coated with alumina layers have been commercially available for over two decades. The CVD technique usually employed involves the deposition of material from a reactive gas atmosphere on a substrate surface held at elevated temperatures. $Al_2O_3$ crystallizes into several different phases such as $\alpha$(alpha), $\kappa$(kappa) and $\chi$(chi) called the "$\alpha$-series" with hcp (hexagonal close packing) stacking of the oxygen atoms, and into $\gamma$(gamma), $\theta$(theta), $\eta$(eta) and $\delta$(delta) called the "$\gamma$-series" with fcc (face centered cubic) stacking of the oxygen atoms. The most often occurring $Al_2O_3$-phases in CVD coatings deposited on cemented carbides at conventional CVD temperatures, 1000-1050°C, are the stable alpha and the metastable kappa phases,

however, occasionally the metastable theta phase has also been observed.

The CVD $Al_2O_3$-coatings of the α-, κ- and/or θ-phase are fully crystalline with a grain size in the range of 0.5-5 µm and having well-facetted grain structures.

The inherently high deposition temperature of about 1000°C renders the total stress in CVD $Al_2O_3$-coatings on cemented carbide substrates to be tensile, hence the total stress is dominated by thermal stresses caused by the difference in thermal expansion coefficients between the substrate and the coating and less by intrinsic stresses which have their origin from the deposition process itself and are of compressive nature. The tensile stresses may exceed the rupture limit of $Al_2O_3$ and cause the coating to crack extensively and thus degrade the performance of the cutting edge in e.g. wet machining where the corrosive chemicals in the coolant fluid may exploit the cracks in the coating as diffusion paths.

Generally CVD-coated tools perform very well when machining various steels and cast irons under dry or wet cutting conditions. However, there exists a number of cutting operations or machining conditions when PVD-coated tools are more suitable e.g. in drilling, parting and threading and other operations where sharp cutting edges are required. Such cutting operations are often referred to as the "PVD coated tool application area".

Plasma assisted CVD technique, PACVD, makes it possible to deposit coatings at lower substrate temperatures as compared to thermal CVD temperatures and thus avoid the dominance of the thermal stresses. Thin $Al_2O_3$ PACVD films, free of cracks, have been deposited on cemented carbides at substrate temperatures 450-700°C (DE 41 10 005, DE 41 10 006, DE 42 09 975). The PACVD process for depositing $Al_2O_3$ includes the reaction between

an Al-halogenide, e.g. $AlCl_3$, and an oxygen donor, e.g. $CO_2$, and because of the incompleteness of this chemical reaction, chlorine is trapped in the $Al_2O_3$-coating and its content could be as large as 3.5 %. Furthermore, these PACVD $Al_2O_3$-coatings are generally composed of, besides the crystalline alpha- and/or gamma-$Al_2O_3$-phase, a substantial amount of amorphous alumina which in combination with the high content of halogen impurities, degrades both the chemical and mechanical properties of said coating, hence making the coating material non-optimised as a tool material.

The field of the present invention relates particularly to the art of PVD $Al_2O_3$ coated cutting tools used in metal machining.

There exist several PVD techniques capable of producing refractory thin films on cutting tools and the most established methods are ion plating, DC- and RF-magnetron sputtering, arc discharge evaporation, IBAD (Ion Beam Assisted Deposition) and Activated Reactive Evaporation (ARE). Each method has its own merits and the intrinsic properties of the produced coatings such as microstructure/grain size, hardness, state of stress, intrinsic cohesion and adhesion to the underlying substrate may vary depending on the particular PVD method chosen. Early attempts to PVD deposit $Al_2O_3$ at typical PVD temperatures, 400-500°C, resulted in amorphous alumina layers which did not offer any notable improvement in wear resistance when applied on cutting tools. PVD deposition by HF diode or magnetron sputtering resulted in crystalline $\alpha$-$Al_2O_3$ only when the substrate temperature was kept as high as 1000 °C (Thornton and Chin, Ceramic Bulletin, 56(1977)504). Likewise, applying the ARE method for depositing $Al_2O_3$, only resulted in fully dense and hard $Al_2O_3$-coatings at substrate temperatures

around 1000°C (Bunshah and Schramm, Thin Solid Films, 40(1977)211).

With the invention of the bipolar pulsed DMS technique (Dual Magnetron Sputtering) which is disclosed in DD 252 205 and DE 195 18 779, a wide range of opportunities opened up for the deposition of insulating layers such as $Al_2O_3$ and, furthermore, the method has made it possible to deposit crystalline $Al_2O_3$-layers at substrate temperatures in the range of 500 to 800°C. In the bipolar dual magnetron system, the two magnetrons alternately act as an anode and a cathode and, hence, preserve a metallic anode over long process times. At high enough frequencies, possible electrical charging on the insulating layers will be suppressed and the otherwise troublesome phenomenon of "arcing" will be limited. Hence, according to DE 195 18 779, the DMS sputtering technique is capable of depositing and producing high-quality, well-adherent, crystalline $\alpha$-$Al_2O_3$ thin films at substrate temperatures less than 800°C. The "$\alpha$-$Al_2O_3$-layers", with a typical size of the $\alpha$-grains varying between 0.2 and 2 µm, may partially also contain the gamma($\gamma$) phase from the "$\gamma$-series" of the $Al_2O_3$-polymorphs. The size of the $\gamma$-grains in the coating is much smaller than the size of the $\alpha$-grains. The $\gamma$-$Al_2O_3$ grain size typically varies between 0.05 and 0.1 µm. In the $Al_2O_3$-layers where both modifications of $\gamma$ and $\alpha$-phase were found, the $\gamma$-$Al_2O_3$-phase showed a preferred growth orientation with a (440)-texture. When compared to prior art plasma assisted deposition techniques such as PACVD as described in DE 42 09 975, the novel, pulsed DMS sputtering deposition method has the decisive, important advantage that no impurities such as halogen atoms, e.g. chlorine, are incorporated in the $Al_2O_3$-coating.

According to the present invention there is provided an improved method of depositing a hard and wear

resistant $\gamma$-$Al_2O_3$ layer by pulsed magnetron sputtering at substrate temperatures of 400 to 700°C, preferably 500 to 600°C on a cutting tool for metal machining such as turning (threading and parting), milling and drilling. Said cutting tool comprises a body of a hard material such as cemented carbide, cermets, ceramics, high speed steel or a superhard material such as cubic boron nitride and/or diamond. The $\gamma$-$Al_2O_3$-layers consist of high-quality, dense, fine-grained crystalline $Al_2O_3$ with a grain size less than 0.1 µm and they are virtually free of cracks and halogen impurities.

The $\gamma$-$Al_2O_3$-layer may be included in a wear resistant coating composed of one or more layers of refractory compounds at which the $\gamma$-$Al_2O_3$-layer preferably is the outermost layer and the innermost layer(s), if any at all, between the tool body and the $Al_2O_3$-layer, is composed of metal nitrides, carbonitrides and/or carbides with the metal elements selected from Ti, Nb, Hf, V, Ta, Mo, Zr, Cr, W and Al.

In contrast to the state of the art, the $\gamma$-$Al_2O_3$-layers according to the invention further give the cutting edges of the tool an extremely smooth surface finish which, compared to prior art $\alpha$-$Al_2O_3$ coated tools, results in an improved surface finish also of the work-piece being machined. The very smooth surface finish can be attributed to the very fine crystallinity of the coating. The "$\gamma$-$Al_2O_3$"-layers may also partially contain other phases from the "$\gamma$-series" like $\theta$, $\delta$ and $\eta$.

The fine-grained, crystalline $\gamma$-$Al_2O_3$ according to the invention is strongly textured in the [440]-direction, A Texture Coefficient, TC, can be defined as:

$$TC(hkl) = \frac{I(hkl)}{I_o(hkl)} \left\{\frac{1}{n} \sum \frac{I(hkl)}{I_o(hkl)}\right\}^{-1}$$

where

I(hkl) = measured intensity of the (hkl) reflection

$I_o$(hkl) = standard intensity from the ASTM standard powder pattern diffraction data

n = number of reflections used in the calculation

(hkl) reflections used are: (111), (311), (222), (400) and (440) and whenever the TC(hkl)>1, there is a texture in the [hkl]-direction. The larger the value of TC(hkl), the more pronounced is the texture. According to the present invention, the TC for the set of (440) crystal planes is greater than 1.5.

When the very fine-grained $\gamma$-$Al_2O_3$ coated cemented carbide cutting tools according to the invention are used in the machining of steel or cast iron, several important improvements compared to prior art have been observed. Surprisingly, the PVD $\gamma$-$Al_2O_3$ without containing any portion of the coarser and thermodynamically stable $\alpha$-$Al_2O_3$-phase, shows in certain metal machining operations, a wear resistance which is equal to the wear resistance found in coarser CVD $\alpha$-$Al_2O_3$-coatings deposited at temperatures around 1000 °C. Furthermore, the fine-grained PVD $\gamma$-$Al_2O_3$-coatings show a wear resistance considerably better than prior art PVD-coatings. These observations open up the possibility to considerably improve the cutting performance and prolong the tool lives of PVD coated tools. The low deposition temperature will also make it possible to deposit PVD $\gamma$-$Al_2O_3$-coatings on high-speed steel tools.

A further improvement in cutting performance can be anticipated if the edges of the $\gamma$-$Al_2O_3$ coated cutting tools according to the invention are treated by a gentle wet-blasting process or by edge brushing with brushes based on e.g. SiC as disclosed in US 5,861,210.

The total coating thickness according to the present invention varies between 0.5 and 20 µm, preferably between 1 and 15 µm with the thickness of the non-$Al_2O_3$-

layer(s) varying between 0.1 and 10 µm, preferably between 0.5 and 5 µm. The fine-grained $\gamma$-$Al_2O_3$-coating can also be deposited directly onto the cutting tool substrate and the thickness of said $\gamma$-$Al_2O_3$ varies then between 0.5 and 15 µm preferably between 1 and 10 µm. Similarly, further layers of metal nitrides and/or carbides with the metal elements selected from Ti, Nb, Hf, V, Ta, Mo, Zr, Cr, W and Al can be deposited on top of the $Al_2O_3$-layer.

The $\gamma$-$Al_2O_3$ layer according to the invention is deposited by pulsed magnetron sputtering at a substrate temperature of 400-700°C, preferably 500-600°C, using aluminium targets and a mixture of at least one rare and at least one reactive gas, preferably argon and oxygen. A preferred solution to carry out the pulsed magnetron sputtering process is the usage of a Dual Magnetron System (DMS). Additionally, the process according to the invention is characterized in cyclic interruptions of the flux of particles impinging onto each individual substrate. This flux consists of neutrals, ions, electrons, photons etc. It seems that these interruptions cause renucleation processes resulting in the observed very fine grained structure of the $\gamma$-$Al_2O_3$ layer. One easy way to realize said cyclic interruptions of the flux is to fixture the substrates on a cylindrical basket ahich rotates in front of the magnetrons, hence causing the substrates moving in and out of the plasma deposition zone. The frequency of said cyclic interruptions is between 0.1 and 10 per minute. The duration of the interruption of the flux of the impinging particles is at least 10 % of the duration of the whole period. Alternatively, the cyclic interruption of the flux of impinging particles occurs aperiodically. A further characteristics of the process consists in setting the flow of the reactive gas for such a value that the im-

pedance of the magnetron discharge lies between 150 % and 250 % of the impedance of a discharge burning between totally oxide-covered target electrodes. This totally oxide-covered state of the targets is indicated by a drastically reduced deposition rate and the presence of oxygen lines in the optical emission spectrum of the plasma. Further, improvement of the microstructure and phase composition of the $\gamma$-$Al_2O_3$ layer will be achieved by applying a bipolar pulsed bias voltage to the substrates during the deposition. This bipolar bias voltage is preferably asymmetric for both polarities with regard to at least one of the parameters voltage level and pulse duration. This leads to an alternating flux of ions and electrons necessary for the cyclic discharge of the growing insulating layer. Preferred is a bias voltage level between 20 and 200 preferably 50 and 100 V at a frequency in the range of 1-5 kHz. Depending on the geometric conditions of the deposition arrangement, an asymmetric bias pulsing with regard to the parameters voltage level and pulse duration can be useful. In this case the duration of the positive polarity should be significantly lower than or at most equal to the duration of the negative polarity. Preferably, the pulse bias frequency lies in the range of 100 Hz to 10 kHz, preferably in the range of 1 kHz to 5 kHz, and the duration of the positive polarity of the substrate is at most equal to, preferably 5 to 20 times lower than the duration of the negative polarity.

The layer(s) described in the present invention, comprising metal nitrides and/or carbides and/or carbonitrides and with the metal elements selected from Ti, Nb, Hf, V, Ta, Mo, Zr, Cr, W and Al can be deposited by PVD-technique, CVD- and/or MTCVD-technique (Medium Temperature Chemical Vapor Deposition).

Example 1

A) Commercially available cemented carbide threading inserts of style R166.OG-16MM01-150 having a composition of 10 w% Co and balance WC, coated with an approximately 2 μm TiN-layer by an ion plating technique.

B) TiN coated tools from A) were coated with a 1 μm fine-grained γ-$Al_2O_3$-layer in a separate experiment with the pulsed magnetron sputtering technique. The deposition temperature was set for 650°C. The total pressure of the gas mixture consisting of argon and oxygen was set for 1.5 μbar. The working point of the reactive magnetron discharge was controlled by the oxygen flow in such a mode that the impedance of the discharge was set to 200% of the impedance measured with totally oxide covered target electrodes of the used DMS. A cyclic interruption of the particle flux towards each individual substrate was realised by rotating an arrangement of substrates and shields in front of a DMS during deposition. During the deposition process a rectangular shaped bipolar pulsed bias voltage of 50 V for both polarities and a frequency of 5 kHz was applied onto the substrates.

Claims

1. A process for producing a coated cutting tool consisting of a coating and a substrate, c h a r a c t e r i s e d in that at least one refractory layer consisting of fine-grained, crystalline γ-$Al_2O_3$ is deposited by reactive magnetron sputtering onto the moving substrate in a vacuum by pulsed magnetron sputtering in a mixture of a rare gas and a reactive gas at a pulse frequency set for 10 to 100 kHz, preferably 20-50 kHz, whereby deposition occurs with a rate of at least 1 nm/s with reference to a stationarily arranged substrate, at a magnetron target power density in time average set for at least 10 $W/cm^2$, substrate temperature set in the range of 400 to 700°C, preferably in the range of 500 to 600 °C, depending on the material of the tool body being coated and the flux of impinging particles onto each individual substrate is cyclically interrupted.

2. A process according to claim 1, c h a r a c t e r i z e d in that the rare gas is argon.

3. A process according to claim 1, c h a r a c t e r i z e d in that the reactive gas is oxygen.

4. A process according to claim 1, c h a r a c t e r i z e d in that the cyclic interruption of the flux of impinging particles occurs periodically with a frequency in the range between 0,1 per minute and 10 per minute.

5. A process according to claims 1 or 4, c h a r a c t e r i z e d in that the duration of the interruption of the flux of the impinging particles is at least 10 % of the duration of the whole period.

6. A process according to claim 1, c h a r a c t e r i z e d in that the cyclic interruption of the flux of impinging particles occurs aperiodically.

7. A process according to at least one of the claims 1 to 6, c h a r a c t e r i z e d in that a bipolar pulsed bias voltage is applied to the substrates.

8. A process according to claim 7 c h a r a c t e r i z e d in that the applied bipolar bias voltage is asymmetric for both polarities with regard to at least one of the parameters voltage level and pulse duration.

9. A process according to claim 7 and 8, c h a r a c t e r i z e d in that the maximum value of bias voltage in each pulse lies in the range of 20 V to 200 V preferably between 50 V and 100 V.

10. A process according to claim 7, c h a r a c t e r i z e d in that the pulse bias frequency lies in the range of 100 Hz to 10 kHz, preferably in the range of 1 kHz to 5 kHz, and the duration of the positive polarity of the substrate is at most equal to, preferably 5 to 20 times lower than the duration of the negative polarity.

11. A process according to claim 1, c h a r a c t e r i z e d in that the flow of the reactive gas is set for such a value that the impedance of the magnetron discharge lies between 150% and 250 % of the impedance of a discharge burning between totally oxide-covered target electrodes.

12. A process according to claim 1, c h a r a c t e r i z e d in that the $Al_2O_3$-layer is deposited by the sputtering of two magnetrons with Al targets that are alternatively switched as a cathode and as a anode of a magnetron sputtering apparatus.

13. A process according to at least one of the claims 9 and 10 c h a r a c t e r i s e d in that additional, non-$Al_2O_3$-layers are also deposited by a PVD process (Physical Vapor Deposition), particularly by pulsed magnetron sputtering.

14. A process according to claim 11, c h a r a c t e r i s e d in that all layers, $Al_2O_3$ and non-$Al_2O_3$-layer(s), are deposited in the same coating apparatus without vacuum interruption.

15. A process of at least one of the claims 9 and 10, c h a r a c t e r i s e d in that additional, non-$Al_2O_3$-layers are applied by a CVD process (Chemical Vapor Deposition).

AMENDED CLAIMS

[received by the International Bureau on 18 September 2000 (18.09.00); original claims 1-15 replaced by new claims 1-8 (3 pages)]

1. A process for producing a coated cutting tool comprising a coating and a substrate of cemented carbide or cermet, ceramic or high speed steel, cubic boron nitride or diamond, whereas said coating comprises a structure of one or more refractory compound layers, wherein at least one refractory layer consisting of fine-grained, crystalline $\gamma$-$Al_2O_3$ with a grainsize less than 0.1 µm is deposited by a reactive, bipolar pulsed magnetron sputtering technique in a mixture of a rare gas and a reactive gas at a pulse frequency set for 10 to 100 kHz, preferably 20-50 kHz, and with a magnetron target power density in time avarage of at least 10 $W/cm^2$, and at a substrate temperature in the range 400 to 700 °C, preferably in the range 500 to 600 °C, depending on the material of the tool body being coated, c h a r a c t e r i z e d in that

- a bipolar pulsed bias voltage is applied to the substrates,
- the flow of reactive gas is set for such a value that the impedance of the magnetron discharge lies between 150% and 250% of the impedance of the discharge burning between totally oxide-covered target electrodes,
- the flux of impinging particles onto each individual substrate is cyclically interupted,
- the deposition occurs with a rate of at least 1 nm/s with reference to a stationary arranged substrate.

2. A process according to claim 1, c h a r a c - t e r i z e d in that the rare gas is argon.

3. A process according to claim 1, c h a r a c - t e r i z e d in that the reactive gas is oxygen.

4. A process according to at least one of the claims 1 -3, c h a r a c t e r i z e d in that

- the bipolar pulsed bias frequency applied to the substrates is set for 0.1 to 10 kHz, preferably 1 to 5 kHz,

- the duration of the positive bias voltage pulse on the substrates is at most equal to, preferably 5 to 20 times shorter, than the duration of the negative bias voltage pulse,

- the applied bipolar bias voltage is asymmetric for both polarities with regard to at least one of the parameters voltage level and pulse duration,

- the maximum value of the bias voltage in each pulse is set for 20 to 200 V, preferably 50 to 100 V.

5. A process according to claim 4, c h a r a c -

t e r i z e d in that the flux of impinging particles on the substrates occurs periodically with a frequency in the range 0.1 per minute and 10 per minute, and the duration of the interruption of the flux is at least 10% of the duration of the whole period.

6. A process according to claim 4, c h a r a c - t e r i z e d in that the cyclic interruption of the flux of impinging particles occurs aperiodically.

7. A process according to claims 4 - 7, c h a r a c t e r i z e d in that the additional non-alumina layers are also deposited by a Physical Vapor Deposition (PVD) process, particularly by pulsed magnetron sputtering.

8. A process according to claim 7, c h a r a c - t e r i z e d in that all the layers are deposited in the same coater without vacuum interruption.

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 00/00857

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC7: C23C 14/08, C23C 14/35, C23C 28/04 // B23B 27/14

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C23C, C04B, B23B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPIL, EDOC, JAPIO, INSPEC, EI COMPENDEX, METADEX, PASCAL, ENERGY SCITEC, CA

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | Surface and Coatings Technology, Volume 86-87, 1996, F.Fietzke et al, "The deposition of hard crystalline A12O3 layers by means of bipolar pulsed magnetron sputtering", page 657 - page 663, see especially abstract, page 659-662<br>-- | 1-15 |
| A | Surface and Coatings Technology, Volume 82, 1996, O. Zywitzki et al, "Effect of the substrate temperature on the structure and properties of A12O3 layers reactively deposited by pulsed magnetron sputtering", page 169 - page 175, see especielly page 169 - 171 and page 173<br>-- | 1-15 |

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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# INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | US 5516588 A (HENDRIKUS VAN DEN BERG ET AL), 14 May 1996 (14.05.96), column 6, line 45 - line 67 | 15 |

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Information on patent family members

02/12/99

International application No.
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